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# The Chemistry of Carbon

## Part I (Structural)

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P. N. CALCRAFT

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*Director:*
R. T. Slattery, B.Sc., A.S.T.C., A.R.A.C.I., M.A.C.E.

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NATIONAL SCIENCE CURRICULUM MATERIALS

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# The Chemistry of Carbon

## Part I (Structural)

P. N. Calcraft
*Matriculation College, Launceston, Tasmania*

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# PERIODIC TABLE

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 H 1.008 | | | | | | | | | | | | | | | | | 2 He 4.00 |
| 3 Li 6.94 | 4 Be 9.01 | | | | | | | | | | | 5 B 10.8 | 6 C 12.01 | 7 N 14.01 | 8 O 16.00 | 9 F 19.0 | 10 Ne 20.2 |
| 11 Na 23.0 | 12 Mg 24.3 | | | | | | | | | | | 13 Al 27.0 | 14 Si 28.1 | 15 P 31.0 | 16 S 32.1 | 17 Cl 35.5 | 18 Ar 39.9 |
| 19 K 39.1 | 20 Ca 40.1 | 21 Sc 45.0 | 22 Ti 47.9 | 23 V 50.9 | 24 Cr 52.0 | 25 Mn 54.9 | 26 Fe 55.8 | 27 Co 58.9 | 28 Ni 58.7 | 29 Cu 63.5 | 30 Zn 65.4 | 31 Ga 69.7 | 32 Ge 72.6 | 33 As 74.9 | 34 Se 79.0 | 35 Br 79.9 | 36 Kr 83.8 |
| 37 Rb 85.5 | 38 Sr 87.6 | 39 Y 88.9 | 40 Zr 91.2 | 41 Nb 92.9 | 42 Mo 95.9 | 43 Tc (99) | 44 Ru 101.1 | 45 Rh 102.9 | 46 Pd 106.4 | 47 Ag 107.9 | 48 Cd 112.4 | 49 In 114.8 | 50 Sn 118.7 | 51 Sb 121.8 | 52 Te 127.6 | 53 I 126.9 | 54 Xe 131.3 |
| 55 Cs 132.9 | 56 Ba 137.3 | 57-71 La-Lu | 72 Hf 178.5 | 73 Ta 180.9 | 74 W 183.9 | 75 Re 186.2 | 76 Os 190.2 | 77 Ir 192.2 | 78 Pt 195.1 | 79 Au 197.0 | 80 Hg 200.6 | 81 Tl 204.4 | 82 Pb 207.2 | 83 Bi 209.0 | 84 Po (210) | 85 At (210) | 86 Rn (222) |
| 87 Fr (223) | 88 Ra (226) | 89-103 Ac-Lw | 104 | 105 | | | | | | | | | | | | | |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 57 La 138.9 | 58 Ce 140.1 | 59 Pr 140.9 | 60 Nd 144.2 | 61 Pm (145) | 62 Sm 150.4 | 63 Eu 152.0 | 64 Gd 157.2 | 65 Tb 158.9 | 66 Dy 162.5 | 67 Ho 164.9 | 68 Er 167.3 | 69 Tm 168.9 | 70 Yb 173.0 | 71 Lu 175.0 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 89 Ac (227) | 90 Th 232.0 | 91 Pa (231) | 92 U 238.0 | 93 Np (237) | 94 Pu (242) | 95 Am (243) | 96 Cm (248) | 97 Bk (247) | 98 Cf (249) | 99 Es (254) | 100 Fm (253) | 101 Md (256) | 102 No (254) | 103 Lw (257) |

*Parenthetical values are mass numbers of the isotopes with longest half lives*

## INTERNATIONAL ATOMIC WEIGHTS

*(Atomic Weights relative to $^{12}C = 12$ exactly)*

| *Atomic Number* | *Name* | *Symbol* | *Atomic Weight* | *Atomic Number* | *Name* | *Symbol* | *Atomic Weight* |
|---|---|---|---|---|---|---|---|
| 1 | Hydrogen | H | 1.008 | 31 | Gallium | Ga | 69.72 |
| 2 | Helium | He | 4.003 | 32 | Germanium | Ge | 72.59 |
| 3 | Lithium | Li | 6.939 | 33 | Arsenic | As | 74.92 |
| 4 | Beryllium | Be | 9.012 | 34 | Selenium | Se | 78.96 |
| 5 | Boron | B | 10.81 | 35 | Bromine | Br | 79.91 |
| 6 | Carbon | C | 12.01 | 36 | Krypton | Kr | 83.80 |
| 7 | Nitrogen | N | 14.01 | 37 | Rubidium | Rb | 85.47 |
| 8 | Oxygen | O | 16.00 | 38 | Strontium | Sr | 87.62 |
| 9 | Fluorine | F | 19.00 | 39 | Yttrium | Y | 88.91 |
| 10 | Neon | Ne | 20.18 | 40 | Zirconium | Zr | 91.22 |
| 11 | Sodium | Na | 22.99 | 41 | Niobium | Nb | 92.91 |
| 12 | Magnesium | Mg | 24.31 | 42 | Molybdenum | Mo | 95.94 |
| 13 | Aluminium | Al | 26.98 | 43 | Technetium* | Tc | (99) |
| 14 | Silicon | Si | 28.09 | 44 | Ruthenium | Ru | 101.1 |
| 15 | Phosphorus | P | 30.97 | 45 | Rhodium | Rh | 102.9 |
| 16 | Sulphur | S | 32.06 | 46 | Palladium | Pd | 106.4 |
| 17 | Chlorine | Cl | 35.45 | 47 | Silver | Ag | 107.9 |
| 18 | Argon | Ar | 39.95 | 48 | Cadmium | Cd | 112.4 |
| 19 | Potassium | K | 39.10 | 49 | Indium | In | 114.8 |
| 20 | Calcium | Ca | 40.08 | 50 | Tin | Sn | 118.7 |
| 21 | Scandium | Sc | 44.96 | 51 | Antimony | Sb | 121.8 |
| 22 | Titanium | Ti | 47.90 | 52 | Tellurium | Te | 127.6 |
| 23 | Vanadium | V | 50.94 | 53 | Iodine | I | 126.9 |
| 24 | Chromium | Cr | 52.00 | 54 | Xenon | Xe | 131.3 |
| 25 | Manganese | Mn | 54.94 | 55 | Caesium | Cs | 132.9 |
| 26 | Iron | Fe | 55.85 | 56 | Barium | Ba | 137.3 |
| 27 | Cobalt | Co | 58.93 | 57 | Lanthanum | La | 138.9 |
| 28 | Nickel | Ni | 58.71 | 58 | Cerium | Ce | 140.1 |
| 29 | Copper | Cu | 63.54 | 59 | Praseodymium | Pr | 140.9 |
| 30 | Zinc | Zn | 65.37 | 60 | Neodymium | Nd | 144.2 |

*Unstable elements

*Parenthetical numbers refer to the mass number (not the atomic weight) of the isotope with the longest half-life.*

## INTERNATIONAL ATOMIC WEIGHTS

*(Atomic Weights relative to $^{12}C = 12$ exactly)*

| *Atomic Number* | *Name* | *Symbol* | *Atomic Weight* |
|---|---|---|---|
| 61 | Promethium* | Pm | (145) |
| 62 | Samarium | Sm | 150.4 |
| 63 | Europium | Eu | 152.0 |
| 64 | Gadolinium | Gd | 157.3 |
| 65 | Terbium | Tb | 158.9 |
| 66 | Dysprosium | Dy | 162.5 |
| 67 | Holmium | Ho | 164.9 |
| 68 | Erbium | Er | 167.3 |
| 69 | Thulium | Tm | 168.9 |
| 70 | Ytterbium | Yb | 173.0 |
| 71 | Lutetium | Lu | 175.0 |
| 72 | Hafnium | Hf | 178.5 |
| 73 | Tantalum | Ta | 180.9 |
| 74 | Tungsten | W | 183.9 |
| 75 | Rhenium | Re | 186.2 |
| 76 | Osmium | Os | 190.2 |
| 77 | Iridium | Ir | 192.2 |
| 78 | Platinum | Pt | 195.1 |
| 79 | Gold | Au | 197.0 |
| 80 | Mercury | Hg | 200.6 |
| 81 | Thallium | Tl | 204.4 |
| 82 | Lead | Pb | 207.2 |
| 83 | Bismuth | Bi | 209.0 |
| 84 | Polonium* | Po | (210) |
| 85 | Astatine* | At | (210) |

| *Atomic Number* | *Name* | *Symbol* | *Atomic Weight* |
|---|---|---|---|
| 86 | Radon* | Rn | (222) |
| 87 | Francium* | Fr | (223) |
| 88 | Radium* | Ra | (226) |
| 89 | Actinium* | Ac | (227) |
| 90 | Thorium* | Th | 232.0 |
| 91 | Protactinium* | Pa | (231) |
| 92 | Uranium* | U | 238.0 |
| 93 | Neptunium* | Np | (237) |
| 94 | Plutonium* | Pu | (242) |
| 95 | Americium* | Am | (243) |
| 96 | Curium* | Cm | (248) |
| 97 | Berkelium* | Bk | (247) |
| 98 | Californium* | Cf | (249) |
| 99 | Einsteinium* | Es | (254) |
| 100 | Fermium* | Fm | (253) |
| 101 | Mendelevium* | Md | (256) |
| 102 | Nobelium* | No | (254) |
| 103 | Lawrencium* | Lw | (257) |
| 104 | (Kurchatovium) | | |

*Unstable elements

*Parenthetical numbers refer to the mass number (not the atomic weight) of the isotope with the longest half-life.*

After completing this unit, you should know about, and understand:

- the chemistry of carbon compared with that of the other elements in Group IV of the periodic table;
- the methods used to elucidate the structure of carbon compounds;
- isomerism;
- the importance of functional groups in organic chemistry;
- the system of nomenclature used in organic chemistry;
- the chemistry of some typical functional groups;
- the physical chemistry of four hydrocarbon series; and
- the general properties to be expected in any homologous series.

You should be able to:

- carry out a qualitative analysis on a carbon compound containing C, H, N, S, or halides;
- work out the empirical formula of a carbon compound given the results of its quantitative analysis;
- work out the molecular formula of a carbon compound;
- draw up the possible structural formulas of a carbon compound using simple valence rules;
- name carbon compounds from their formulas; and
- work out the formulas of carbon compounds from their names.

# Introduction

The study of carbon and its compounds, is one of the most fascinating studies in the field of chemistry. The carbon compounds are not only useful to man, but play an important role in the chemistry of living things, both plant and animal. Throughout the ages, and particularly in present times, compounds of carbon have been put to many uses. The ancient dyes of the Phoenecians, the wines and spirits of all ages, the poisons of the Borgias, through to modern drugs, fibres, plastics, detergents, fuels, explosives—all can be compounds of carbon. Manufacture of this wide range of products has led to the growth of a huge chemical industry using as its raw materials such resources as coal, petroleum, natural gas and plant and animal products.

All these resources were originally plant or animal matter and this led to the use of the term **organic chemistry** for the study of compounds containing carbon. Much of today's research is concerned with this study, and the number of new carbon compounds synthesized each year is greater than that of all other known compounds that contain no carbon.

The preparation over many centuries of dyes, wines and spirits would make organic chemistry, as a practical science, possibly the oldest known. Even from the earliest days, chemistry fell into two natural divisions—one, concerned with substances of mineral origin (now known as inorganic chemistry), and the other dealing with substances derived from living organisms (organic chemistry). Just as the inorganic chemist was obsessed with the search for the Philosopher's Stone, a substance which would transmute all base metals into gold, so the organic chemist sought the elixir of Life, a medicine to prolong life and endow immortality. These side issues hindered the development of both these branches as exact sciences.

Very few carbon compounds were known until the sixteenth or seventeenth centuries, when the technique of **pyrolysis,** or heat treatment was introduced and applied to many plant and animal products. This naturally led to the destruction of much of the material, but such discoveries as succinic acid from amber, and benzoic acid from gum benzoin, added to the list of new compounds.

The next important technique was introduced in the eighteenth century by Scheele, a Swedish chemist. He extracted plant and animal products with various liquids at ordinary temperatures and in this way was able to isolate some of the substances originally present in the organic material. The method was adopted by other chemists and resulted in many additions to the list of organic compounds. Amongst these we find urea from urine, malic acid from apples, lactic acid from milk, citric acid from lemons and tartaric acid from grapes.

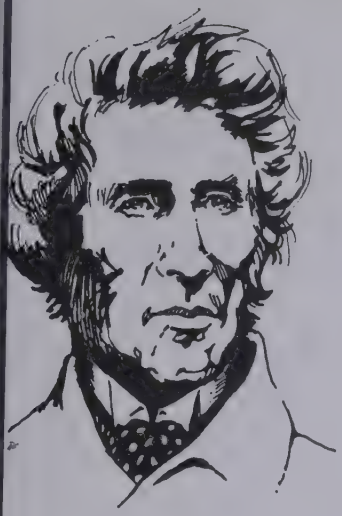
Nothing was known about the composition or structure of these compounds and the first step towards determination came with the combustion experiments of Antoine Lavoisier (1743-1794). By burning organic compounds in an atmosphere of oxygen he nearly always produced carbon dioxide and water, indicating the presence of carbon and hydrogen in the original material. As we shall see later, the measurement of the amount of carbon dioxide and water which is produced from a known amount of original compound, will enable us to calculate the percentage of these elements.

Analytical results produced by this method led to the belief that organic compounds did not obey the laws of simple and multiple proportions. The laws had been formulated from results using materials of mineral origin. Why didn't organic compounds agree with them?

To account for the difference, the scientists of the period said it was due to their association with living objects and that all organic compounds possessed some 'Vital Force' passed to it by the plant or animal.

Surprisingly this belief persisted until the middle of the last century. It was broken only when an organic substance was first prepared from materials of purely mineral origin. The first to accomplish this was Wöhler, a German chemist, who in 1828 synthesized urea from ammonium sulphate and potassium cyanate. At the same time techniques of analysis were improved and chemists were able to show that organic substances did obey the law of multiple proportions even though the proportions were more complicated than normal.

Nowadays we know that organic substances are fundamentally the same as mineral substances and to divide them into a separate group was not justified. The division is retained solely for



FRIEDRICH WÖHLER
(1800-1882)

convenience and a better name for organic chemistry would be the *chemistry of carbon compounds.*

Estimates of the number of carbon compounds vary from five million to six million: they far outnumber the compounds containing any other element. Why is this so? To find the answer we must first look at the chemistry of carbon itself.

## Chemistry

Carbon is the first element of Group IV of the periodic table. It has an atomic number 6 and a mass number 12.00 and thus the normal carbon atom is made up of 6 protons, 6 neutrons and 6 electrons. The atom can be represented by the formula ${}^{12}_{6}C$ where 12 is the mass number and 6 the atomic number.

The nucleus, containing the protons and neutrons, plays no part in the simple chemical reactions of carbon and it is the extra-nuclear electrons, particularly the arrangement of those electrons, which determine the chemical properties. The electronic structure of carbon, and the other elements in Group IV of the periodic table is shown in table 1.

From the data in the table it can be seen that all the elements in Group IV have the same *outer* electronic structure and, as it is the outer electrons which first come into contact with electrons from other atoms, it is these electrons which have the main

*Table 1. The electronic structures of the Group IV elements*

| ELEMENT | SYMBOL | ATOMIC NUMBER | ELECTRONIC STRUCTURE |
|---|---|---|---|
| Carbon | C | 6 | $1s^2 2s^2 2p^2$ |
| Silicon | Si | 14 | $1s^2 2s^2 2p^6 3s^2 3p^2$ |
| Germanium | Ge | 32 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$ |
| Tin | Sn | 50 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$ |
| Lead | Pb | 82 | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^2$ |

influence on the *chemical reactions* of the elements. The similarity in outer electronic structure should therefore lead to a similarity in chemical properties of all the elements of the group.

Like all the other groups in the periodic table there is a decrease in electronegativity as the atomic number increases, and this property is particularly well marked within this group. Carbon and silicon are non-metals, germanium has some metallic properties, tin and lead are typical metals.

Another general characteristic of the periodic table is that the first element in a group differs in many respects from the other members of the group.

This may be explained in terms of the smaller size, higher electronegativity and non-availability of *d*-orbitals associated with the first element. Carbon differs from the other elements in this group in its limitation to a co-ordination number of four, in its unique ability to form multiple bonds such as

$$=C=C=,\ -C\equiv C-,\ =C=O,\ =C=S,\ -C\equiv N$$

and in possessing the property of **catenation.** Catenation is the linking together of identical atoms to form chains and rings. Carbon is characteristic in this respect, with silicon exhibiting catenation to a much smaller extent. Like carbon, silicon has only *s* and *p* electrons (it does possess vacant *d*-orbitals), but the other elements in Group IV possess filled *d*-orbitals and therefore *do not* possess the property of catenation. Thus carbon and silicon differ both from one another and from the rest of the group, but germanium, tin and lead form a well-graded series.

## General Properties of the Group IV Elements

The chief points of resemblance amongst the elements are that they:

(1) all show a covalence of four in at least some of their compounds,
(2) all form an acidic oxide, and
(3) all form a tetrachloride.

### Common Covalence of Four

If the outer electronic structure of the elements is studied, the general pattern is seen to be as in figure 2.

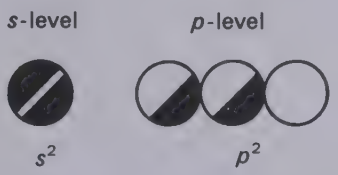



*Figure 2. Outer electronic structure of Group IV elements*

This represents a complete pair of electrons in the *s*-orbital and two single unpaired electrons in each of two, of the three possible, *p*-orbitals.

It would be expected, therefore, that all the elements would show a common valence of two, utilizing the two unshared *p*-electrons, and in fact this does occur in tin (II) and lead (II) compounds. Carbon, on the other hand, always has a covalence of four. The *ground* (or normal) state of the carbon atom is shown in figure 3.

*Figure 3. Ground state of the carbon atom*

On reaction with any other atom, the carbon atom becomes *excited* and has the electronic structure shown in figure 4. (Notice that an electron in the *2s* orbital has been promoted.)

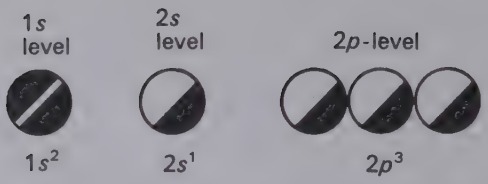



*Figure 4. Excited state of the carbon atom*

This promotion of one of the *2s* electrons to a *2p* orbital means that the carbon atom, on reaction, has four unpaired electrons and so exhibits the expected covalence of four.

Consideration of these four electrons would lead to the expectation that when carbon bonded with other atoms, there would be three bonds alike—formed from the three *p*-electrons of carbon—and one different—formed from the *s*-electron. However, measurement of the angle, strength and length of the bonds in, for example, methane ($CH_4$) shows that all the four bonds are identical. The mechanism of this is not clearly known, and is called **hybridization.** Bonds are formed by overlap of these orbitals with the appropriate orbitals from other atoms. The four orbitals in this case are called $sp^3$ hybrids because they are formed from one *s*-electron and three *p*-electrons and give rise to the tetrahedral structure found in such compounds. Hybridization can occur with other electron orbitals and give rise to different structures (see table 2).

**Formation of an Acidic Oxide**

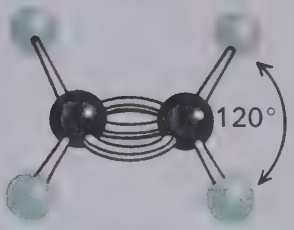
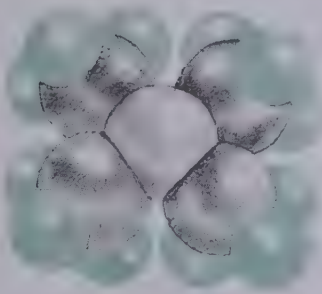
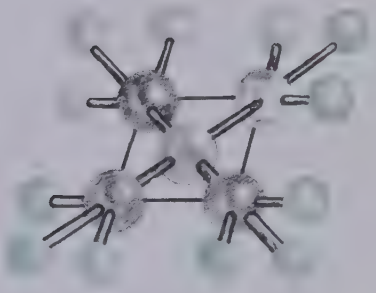
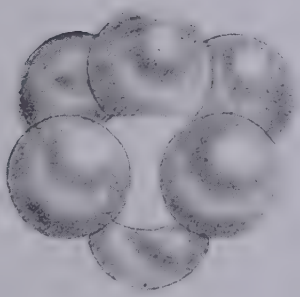
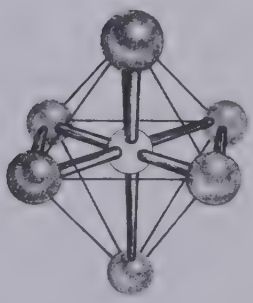
All the elements of this group form an acidic oxide of general formula $XO_2$, e.g. $CO_2$, $PbO_2$. The acidity of this oxide decreases as the atomic number of the Group IV element increases.

Carbon dioxide is a true acid oxide, being the anhydride of carbonic acid.

$$CO_2 + H_2O = H_2CO_3$$

Silicon oxide, or silica, will react only very slowly with water, but readily reacts with alkalis to give silicates. Germanium oxide is less reactive towards alkalis and the tin (IV) oxide and lead (IV) oxide are amphoteric in nature, reacting with both acids and alkalis.

*Table 2. Common types of hybridization*

| Type of hybridization | Example | No. of Bonds | Structure |
|---|---|---|---|
| *sp* | $C_2H_2$ | 2 | LINEAR |
| $sp^2$ | $C_2H_4$ | 3 |   BONDS AT 120° |
| $sp^3$ | $CH_4$ | 4 | TETRAHEDRAL |
| $dsp^2$ |  $[Cu(NH_3)_4]^{2+}$ | 4 |  SQUARE |
| $d^2sp^3$ |  $SF_6$ | 6 |  OCTAHEDRAL |

### Formation of a Tetrachloride

All the elements of the group form a tetrachloride of general formula $XCl_4$, e.g. $CCl_4$, $SnCl_4$. All the tetrachlorides are covalent and have a tetrahedral structure due to $sp^3$ hybridization.

The stability of the tetrachloride decreases with increase in the atomic number of the Group IV element. Since carbon tetrachloride is the most stable it is not hydrolysed in aqueous solutions —the other Group IV tetrachlorides form complex ions on hydrolysis. Hydrolysis or reaction with water, is in this case brought about by boiling with hydrochloric acid which is in effect an aqueous solution of chloride ions.

$$SnCl_4 + 2Cl^-_{(aq)} \rightarrow [SnCl_6]^{2-}$$

### Summary of the Properties of Carbon

In summary, carbon is the first element of Group IV of the periodic table. Although similar in some respects to the other elements in the group, it differs in its great ability to form chains and rings of carbon atoms and in its ability to form multiple bonds. It is these differences that give rise to the vast number of carbon compounds now known. A recent estimate gives the ratio of the number of carbon compounds to the number of other compounds that contain no carbon as twenty to one.

All these different carbon compounds have characteristic properties due to different spatial arrangements within the molecule. It is therefore of great importance that these atomic arrangements, or structures, are known.

## Determination of the Molecular Structure

How do we proceed when we set out to find the structure of any particular compound? The obvious first step is to find what elements the substance contains by carrying out a qualitative analysis; then the amounts of each element present must be determined. This latter information enables an empirical formula to be written which, after determination of the molecular weight, will tell us the number of atoms in each molecule and lead to the

molecular formula. Finally, we can consider the ways in which these atoms are bonded together, and so write a structural formula.

The steps are:
(1) determination of *qualitative composition*,
(2) determination of *quantitative composition*,
(3) calculation of *empirical formula*,
(4) determination of *molecular weight*,
(5) calculation of *molecular formula*, and
(6) determination of *structural formula*.

Now let us consider them in detail.

**Determination of Qualitative Composition**

The qualitative composition simply means the types of elements present in the compound with no indication of the relative amounts. As the elements present in an organic compound are rarely in the ionic form, most tests involve a process for converting the elements into easily detectable ions or into simple, easily-recognized compounds. Luckily only few elements occur in carbon compounds, and the tests employed to show their presence are given below.

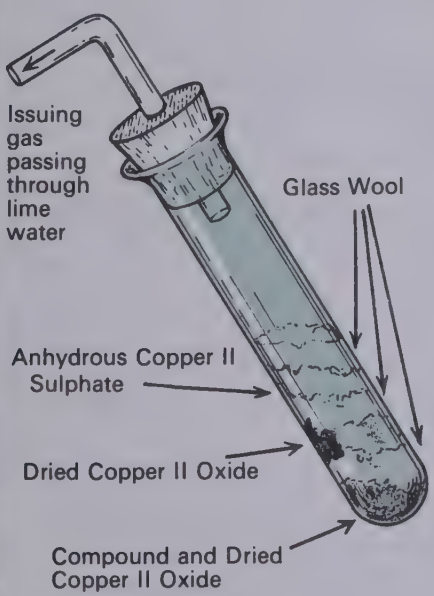

Issuing gas passing through lime water
Glass Wool
Anhydrous Copper II Sulphate
Dried Copper II Oxide
Compound and Dried Copper II Oxide

*Figure 5. Qualitative test for carbon and hydrogen in an organic compound*

(a) *Carbon and Hydrogen*

The presence of carbon can be shown by simply burning the compound in air, when the formation of soot shows carbon is present. A more accurate method involves mixing the substance with carefully dried copper (II) oxide and heating in a hard glass tube. Anhydrous copper (II) sulphate is also placed in the tube (see figure 5).

The carbon is oxidized to carbon dioxide, and detected by bubbling the issuing gas through limewater to give a white precipitate of calcium carbonate:

$$Ca(OH)_2 + CO_2 \quad = \quad CaCO_3 \quad + \quad H_2O$$

ionically:

$$Ca^{2+}_{(aq)} + 2OH^-_{(aq)} + CO_{2(g)} \quad = \quad CaCO_{3(s)} + H_2O_{(l)}$$

The hydrogen is oxidized to water and this changes the anhydrous copper (II) sulphate from white to blue. The copper (II) oxide is the oxidizing agent.

(b) *Nitrogen*

In the *Lassaigne* or *sodium fusion* test the compound is heated with metallic sodium and then dropped into distilled water. This test must be carried out carefully as any unreacted sodium will react violently with water. A less dangerous method is to heat the substance strongly with *Middleton's reagent* and then place the product into distilled water. Middleton's reagent is a finely powdered mixture of anhydrous sodium carbonate (1 part by weight) and zinc dust (2 parts by weight). In each case, any nitrogen in the compound, together with the carbon, combines to form sodium cyanide:

$$N + C + Na \longrightarrow NaCN$$

After the red hot mass is placed in distilled water, the resulting mixture is warmed, filtered, and divided into several parts. A crystal of iron (II) sulphate is added to one part. Reaction takes place to give sodium hexacyanoferrate (II):

$$6NaCN + FeSO_4 \quad = \quad Na_4[Fe(CN)_6] + Na_2SO_4$$

ionically:

$$6CN^-_{(aq)} + Fe^{2+}_{(aq)} \quad = \quad Fe(CN)^{4-}_{6(aq)}$$

Addition of a small amount of dilute sulphuric acid, plus a drop of freshly prepared iron (III) chloride solution, gives a blue precipitate of 'Prussian blue':

$$3Na_4[Fe(CN)_6] + 4FeCl_3 \equiv Fe_4[Fe(CN_6]_3 + 12NaCl$$

or ionically:

$$3Fe(CN)^{4-}_{6(aq)} + 4Fe^{3+}_{(aq)} \equiv Fe_4[Fe(CN)_6]_{3(s)}$$

This blue precipitate confirms the presence of nitrogen in the organic compound.

(c) *Sulphur*

After fusion, any sulphur present in the organic compound is converted either to sodium sulphide or zinc sulphide by reaction with metallic sodium or zinc. The product can be detected in one of two ways:

(i) To a portion of the filtrate obtained after fusion, add a crystal of sodium nitroprusside. A transient reddish-violet colour indicates the presence of sulphur in the original compound.

(ii) If metallic sodium was used for the fusion, acidify another portion of the filtrate with dilute acid, boil gently, and allow the vapours to come into contact with a strip of filter paper moistened with a solution of lead (II) salt.

If sulphur were present in the original compound, a dark brown stain of lead (II) sulphide is produced:

$$Pb^{2+}_{(aq)} + H_2S_{(g)} \equiv PbS_{(s)} + 2H^{+}_{(aq)}$$

If Middleton's reagent is used the *residue* from the original fusion must be used for this test. The residue is acidified and any gas given off tested with the filter paper moistened with a lead (II) salt. A positive result for either test confirms the presence of sulphur in the original compound.

(d) *Halogens*

Any halogen in the organic compound is converted by fusion to sodium halide. This will be present in the filtrate as halide ions. A further portion of the original filtrate is acidified with dilute nitric acid and silver nitrate solution added. A white or yellow

precipitate of silver halide is formed if the original substance contained halide:

$$AgNO_3 + NaX = AgX + NaNO_3$$

ionically:

$$Ag^+_{(aq)} + X^-_{(aq)} = AgX_{(s)}$$

Normal tests (e.g. solubility in ammonium hydroxide) will show which halide was present. If sulphur and/or nitrogen had been detected in the previous tests, it is necessary to boil the solution before adding the silver nitrate. This removes hydrogen sulphide and/or hydrogen cyanide which would also give precipitates with the silver nitrate.

(e) *Metals*

If the presence of metals is suspected, the original compound is strongly heated on a metal spatula. The pyrolysis results in oxidation which gives a residue which can be dissolved in *aqua regia* (1 volume concentrated nitric acid and 3 volumes concentrated hydrochloric acid). Then a routine inorganic cation analysis can be carried out on the solution so formed.

**Determination of Quantitative Composition**

The techniques of quantitative analysis are beyond the scope of this text, but the basic principles are very simple. The carefully weighed sample is burnt in a stream of pure oxygen and as a result *carbon* is converted to carbon dioxide and *hydrogen* to steam. These are then accurately estimated by collecting in suitable absorbents, which are weighed before and after combustion. Any *nitrogen* present is first oxidized in an atmosphere of carbon dioxide, giving oxides of nitrogen which are reduced to pure nitrogen using a hot copper gauze. The amount of nitrogen is measured volumetrically over strong aqueous potassium hydroxide. The latter is present to absorb the carbon dioxide also formed. *Halogens* are estimated as silver halides and *sulphur* as barium sulphate. Until recently there was no positive test for *oxygen*, and the percentage of this element was found by difference, i.e. any percentage of the total composition not accounted for by the above determinations was, allowing for experimental error, assumed to be oxygen.

Modern techniques allow the oxygen to be converted to carbon monoxide using hot carbon. The carbon monoxide is made to react with iodine pentoxide which liberates iodine and the iodine is estimated volumetrically:

$$5CO + I_2O_5 = 5CO_2 + I_2$$

### Calculation of Empirical Formula

Once the qualitative composition has been found, it is possible to calculate the proportions in which the elements are present. The simplest chemical formula capable of expressing these proportions is called the **empirical formula** and the method of calculation is best illustrated using a worked problem.

**PROBLEM**

0.2g of an organic compound gave 0.382g of carbon dioxide and 0.235g of water on complete combustion with oxygen. Calculate the empirical formula of the compound.

### Solution

*Step* 1 Find the percentage of each element present in the compound.

$$\text{wt. of carbon} = \frac{\text{wt. of carbon dioxide} \times \text{atomic wt. carbon}}{\text{molecular wt. carbon dioxide}}$$

$$= 0.3825 \times \frac{12}{44}$$

$$= 0.1043\text{g}$$

$$\% \text{ of carbon} = \frac{\text{wt. of carbon}}{\text{wt. of original sample}} \times 100$$

$$= \frac{0.1043}{0.2} \times 100$$

$$= 52.15\%$$

$$\text{wt. of hydrogen} = \text{wt. of water} \times \frac{\text{molecular wt. hydrogen}}{\text{molecular wt. water}}$$

$$= 0.235 \times \frac{2}{18}$$

$$= 0.0261\text{g}$$

$$\% \text{ of hydrogen} = \frac{\text{wt. of hydrogen}}{\text{wt. of original sample}} \times 100$$

$$= \frac{0.0261}{0.2} \times 100$$

$$= 13.05\%$$

total percentage found

$$= 52.15 + 13.05$$

$$= 65.20\%$$

$\therefore$ percentage oxygen (by difference)

$$= 100 - 65.20$$

$$= 34.80\%$$

*Step* 2 Divide the percentage of each element by the *atomic weight* of the element. This gives the relative number of atoms of the elements present in the compound.

$$\text{carbon} = \frac{52.15}{12} = 4.35$$

$$\text{hydrogen} = \frac{13.05}{1} = 13.05$$

$$\text{oxygen} = \frac{34.8}{16} = 2.175$$

*Step* 3 Divide each number by the smallest number found and then adjust to the nearest whole number. This gives the simplest ratio of the number of atoms present, i.e. the empirical formula.

$$\text{carbon} = \frac{4.35}{2.175} = 2$$

$$\text{hydrogen} = \frac{13.05}{2.175} = 6$$

$$\text{oxygen} = \frac{2.175}{2.175} = 1$$

$\therefore$ The empirical formula of the organic compound is $C_2H_6O$.

**Note** The calculation can be conveniently set out in columns as follows:

| Element | C | H | O |
|---|---|---|---|
| % by weight | 52.15 | 13.05 | 34.80 |
| Atomic weight | 12 | 1 | 16 |
| Relative numbers of atoms | $\frac{52.15}{12} = 4.35$ | $\frac{13.05}{1} = 13.05$ | $\frac{34.80}{16} = 2.175$ |
| Ratio of atoms | $\frac{4.35}{2.175} = 2$ | $\frac{13.05}{2.175} = 6$ | $\frac{2.175}{2.175} = 1$ |

*Conclusion*
Empirical formula of the organic compound is $C_2H_6O$.
The final figures obtained will not always be exact but inspection will show that a particular answer is the obvious one.

**Exercise 1**

Combustion of 0.1562g of an organic compound gave 0.4905g of carbon dioxide and 0.2020g water. Calculate the empirical formula of the compound.

**Determination of Molecular Weight**

After finding the empirical formula we know that the ratio of the atoms of the elements in a molecule of the organic compound is two carbon to six hydrogen to one oxygen. Now we must determine the **molecular weight.** Any suitable method of determination can be used and details of the different methods available may be found by consulting a suitable text. Among methods commonly used are three we will describe.

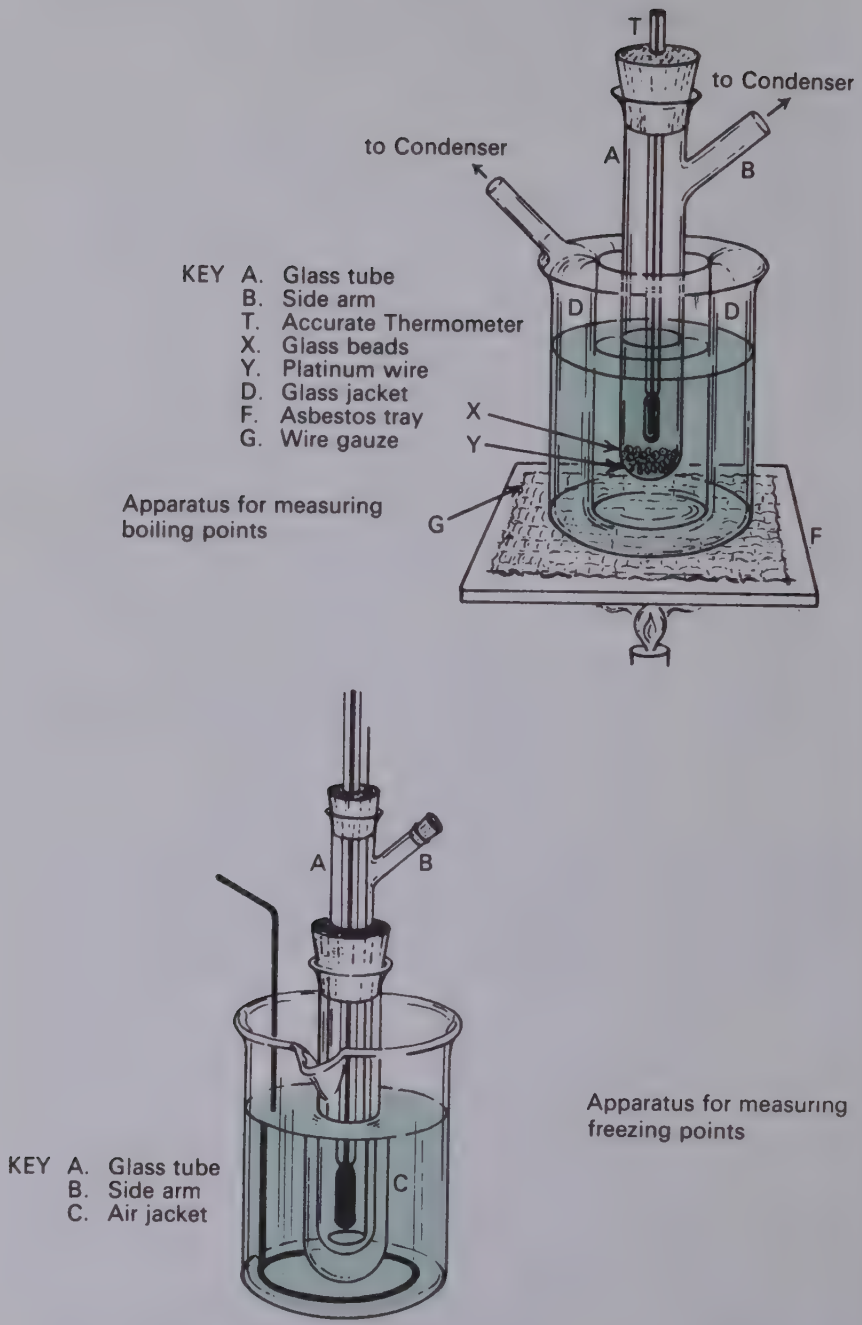



*Figure 6. Apparatus for determination of molecular weight by measurement of boiling or freezing points*

(a) *Victor Meyer's method*
This consists of vaporizing a known amount of liquid, or volatile solid, and measuring the volume and pressure of the vapour formed (or the volume and pressure of an equal volume of displaced air). The volume is converted to standard temperature and pressure, i.e. 760mm mercury pressure and 273 K. Knowing the original weight of the sample, the amount that would occupy 22.4 *l* at S.T.P. can be found, and this will be equal to the molecular weight.

(b) *Boiling point elevation* (*ebulloscopic*) *method*
The boiling point elevation for a given concentration of solute is practically independent of the solvent used. The elevation in a particular solvent depends on the amount of solute added to a definite amount of solvent and is constant for *one mole* of any non-volatile solute in a particular solvent. Measurement of the elevation thus enables the molecular weight to be found.

(c) *Freezing point depression* (*cryroscopic*) *method*
A similar case occurs to that above except that the freezing point of the solution is lower than that of the pure solvent.

**Determination of Molecular Formula**

Once the empirical formula and the molecular weight are known, the **molecular formula** can be found using the relationship:

molecular formula = empirical formula $\times$ $N$ (where $N$ is a whole number)

$$\text{and } N = \frac{\text{molecular weight}}{\text{formula weight}}$$

where formula weight is the sum of the atomic weights as given in the simplest (empirical) formula of the substance. Once again a problem will help you to follow the argument.

**PROBLEM**

An organic liquid was found to have empirical formula $CH_2O$. Determination of the liquid's molecular weight by a cryoscopic (freezing point) method gave a value of approximately 60. Find the molecular formula of the liquid.

$$\text{molecular formula} = \text{empirical formula} \times N$$

$$N = \frac{\text{molecular weight}}{\text{formula weight}} = \frac{60}{12 + (2 \times 1) + 16} = \frac{60}{30} = 2$$

$$\therefore \text{ molecular formula} = CH_2O \times 2$$

$$= C_2H_4O_2$$

Since $N$ must be a whole number, minor inaccuracies in the value used for the molecular weight will not concern us.

### Exercise 2

A certain organic compound is found by analysis to contain 31.9% carbon and 5.3% hydrogen. Further analysis showed that the only other element present is chlorine. When a 1.50 g sample of the compound is converted to vapour it is found to occupy 410 ml at 100°C and 762 mm mercury pressure. Find the empirical formula and molecular formula of the compound.

### Determination of Structural Formula

Having established the molecular formula of the compound the arrangement of the atoms in space needs to be determined. This is represented by the **structural formula** of the compound.

Take the case of the substance having molecular formula $C_2H_6O$. How many ways can we arrange these atoms? Using the known valence of carbon, oxygen and hydrogen (4, 2 and 1 respectively) it is possible to write theoretical structural formulas for the compound. Trial and error will show that only two possibilities exist, namely:

Note that all the four valences of the carbon atoms are satisfied by single covalent bonds. Compounds such as this are called **saturated** compounds.

An alternate way of writing these structures which does not keep emphasizing the fact that the atoms are joined by single bonds is

$CH_3CH_2OH$ and $CH_3OCH_3$

The main difference between the two structures for this compound $C_2H_6O$ is that the oxygen atom is bonded either to two carbon atoms or to one carbon atom only. Compounds like this, which have the same molecular formula but different structural formulas are called **isomers.**

One of the substances with molecular formula $C_2H_6O$ is found to be a sweet smelling liquid called ethanol, the other a sweet smelling gas called methoxymethane (dimethyl ether). It now remains to find which structural formula belongs to which compound. How can we do this? Because it is easier to work with a liquid, it is more convenient to study the chemical properties of ethanol.

If a small piece of clean sodium metal is dropped into the liquid, hydrogen is produced. Evaporation of excess liquid leaves a white crystalline solid which can be shown to have molecular formula $C_2H_5ONa$ (sodium ethoxide). This means that one atom of hydrogen has been replaced by one atom of sodium and, no matter what amounts or conditions are used, no further reaction can be made to take place.

Quantitative measurements of the amounts involved in the reaction enable a balanced equation to be written:

$$C_2H_6O + Na = C_2H_5ONa + \tfrac{1}{2}H_2$$

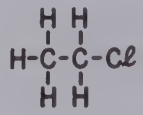
This reaction suggests that *one* hydrogen atom in the molecule differs from all the other hydrogen atoms. Which structure does this evidence support?

If the original liquid is made to react with hydrogen chloride a new compound is formed whose molecular formula can be shown to be $C_2H_5Cl$ (chloroethane). This time one hydrogen and one oxygen atom have been replaced by a chlorine atom. Both the reactions considered involve replacement of atoms by other atoms and are called *substitution* reactions. In reactions of this type intra-molecular rearrangements of the molecule rarely take place.

The equation for the second reaction can be written as:

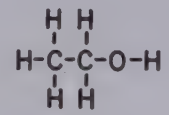
$$C_2H_6O + HCl = C_2H_5Cl + H_2O$$

Using bonding rules it is possible to write only *one* graphic formula for the compound $C_2H_5Cl$ and that is:



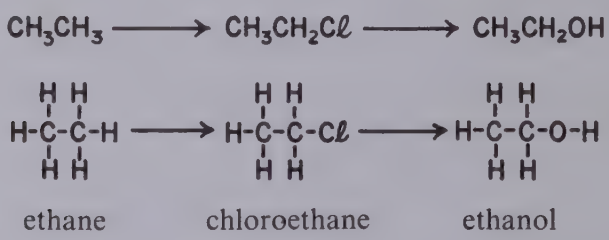

or $CH_3CH_2Cl$

This reaction again supports the suggestion that there is one different hydrogen atom in the molecule and also that it is bonded to the oxygen atom. Which structure does this support? The answer is that both reactions can only be accounted for satisfactorily if the structure of the liquid is:




or $CH_3CH_2OH$

Further confirmation for this structure is obtained by synthesizing ethanol from ethane, via chloroethane. For each compound we can draw only *one* structural formula that satisfies the rules of valence.




Practice at working out these structural formulas is required and models can be of considerable assistance in this respect. *Because a formula which satisfies the rules of valence can be worked out, it must not necessarily be assumed that such a compound is capable of existence.*

The attempt to establish the structural formula of ethanol involved chemical reactions only. Other evidence could have been

used as well, for example, infra-red spectrum studies, X-ray diffraction patterns and ultra-violet spectrum studies. These are the tools of the modern scientist, and further developments are continually taking place in this field. No one fact is sufficient to give absolute proof of a particular structure, but even with the most complicated molecules a pattern of evidence can be built up which favours one of the possibilities more than any other.

## Summary of Determination of Structural Formula

We have seen that for any new compound, a whole sequence of investigations must be carried out before we can be confident of its structure.

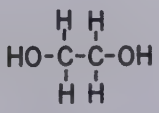
Determination of qualitative and quantitative composition leads to the *empirical formula* which is the simplest chemical formula capable of expressing the proportions in which the elements are present.

Determination of molecular weight enables calculation of the *molecular formula*. This tells us the actual number of atoms of each present.

Use of the rules of valence means we can draw up possible *graphic formulas*. Detailed study of chemical and physical properties tells us the true *structural formula*.

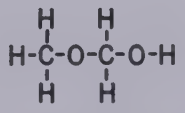
For example, ethylene glycol has empirical formula $CH_3O$ and molecular formula $C_2H_6O_2$. Possible structural formulas are given below:

**a.**



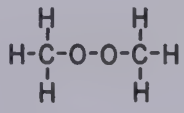
$HOCH_2CH_2OH$

**b.**



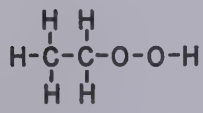
$CH_3OCH_2OH$

**c.**



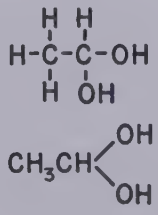
$CH_3O\ O\ CH_3$

**d.**

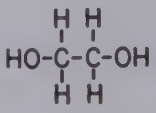


$CH_3CH_2O\ OH$

**e.**



Study of the chemical reactions and physical properties, and finally synthesis by an unambiguous route, shows the structural formula to be:



## Isomerism

It has been seen that *one* molecular formula may represent several different structural formulas. This property is widespread in organic chemistry because of the following two problems:

(a) *the different possibilities by which carbon atoms may link to one another, and*

(b) *the three-dimensional nature of the molecules which enables the same atoms to have different arrangements in space.*

The property is known as **isomerism,** and the different compounds with the same molecular formula are known as **structural isomers.** A structural isomer is therefore one of a number of compounds which contain the same number of each kind of atom, but differ in regard to which atoms are linked to one another, or to the arrangement of those atoms in space.

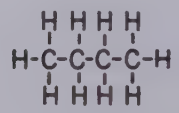
The more atoms there are in a molecule, the more possible isomers there are.

$C_4H_{10}$ exists in *two* isomeric forms

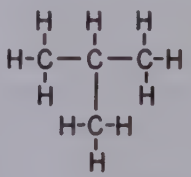
$C_5H_{12}$ exists in *three* isomeric forms

and for $C_{13}H_{28}$ it is possible to write 802 theoretical structures!

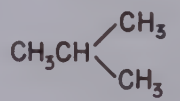
Taking the case of $C_4H_{10}$ the two possible structures are



and

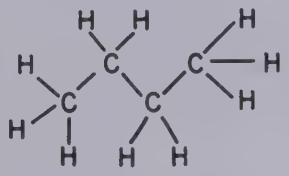


$CH_3CH_2CH_2CH_3$



The substance with molecular formula $C_4H_{10}$ is called butane, and to distinguish between the two structural isomers, the straight chain compound **a** is called normal butane (*n*-butane), and the branched chain compound **b** is called 2-methyl propane or *iso*-butane (see section on Nomenclature).

Because we are working in only one plane on paper, whereas the molecules are actually three dimensional, difficulty is sometimes experienced in representing the structures. In particular one point may cause confusion. Although the normal compounds possess straight chains, in terms of the above definition, their molecules are in fact far from straight as you will see if you handle molecular models. The carbon chain could possibly adopt any random shape, although in practice certain factors such as charge repulsion determine the shape. The molecule of *n*-butane, for instance, is more correctly represented by the following structure:



Models are most helpful in this respect, and for the examples we have encountered so far, three-dimensional representation is shown in the following (figures 7 and 8).

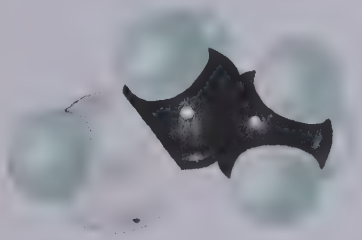


*Figure 7. Three-dimensional representation of ethanol*

Figures 7 and 8 represent compounds which are examples of **position isomerism,** or substitution isomerism, where the isomers differ from each other in the position occupied by a particular atom, or group of atoms.

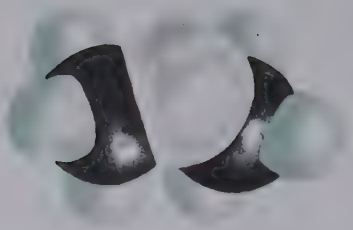


*Figure 8. Three-dimensional representation of methoxymethane (dimethyl ether)*

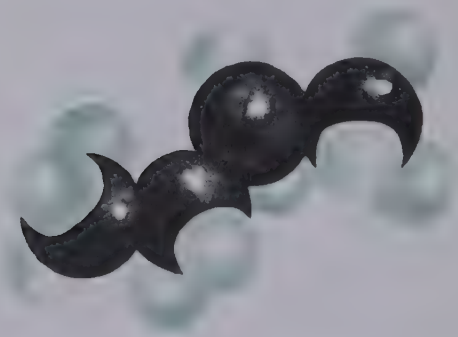


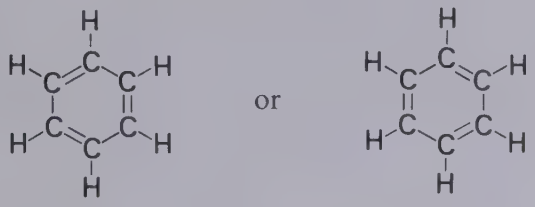
*Figure 9. Three-dimensional representation of n-butane*

*Figure 10. Three-dimensional representation of 2-methyl propane (iso-butane)*

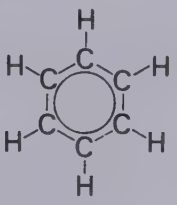
Figures 9 and 10 represent compounds which are examples of **chain isomerism.** Chain isomerism depends upon the way in which a chain of carbon atoms are linked together.

Position, or substitution, isomerism often occurs amongst *aromatic* compounds. All the examples introduced so far have

been *aliphatic* compounds. Aliphatic compounds are those containing straight, or branched, chains of carbon atoms. Aromatic compounds contain rings of carbon atoms and are derived from the hydrocarbon *benzene*. Benzene has molecular formula $C_6H_6$. The structure formula is often written as:




Neither of these formulas is correct because the double bonds in benzene are not localized, that is, they are not in a set position, but are shared with the whole of the molecule. A better representation of the structure would be:



Compounds which contain multiple bonds between atoms are called **unsaturated compounds.**

An example of position isomerism amongst these aromatic compounds is shown by chloromethyl benzene (chlorotoluene). The molecular formula of this compound is $C_7H_7Cl$. The possible structural isomers are shown in figure 11.

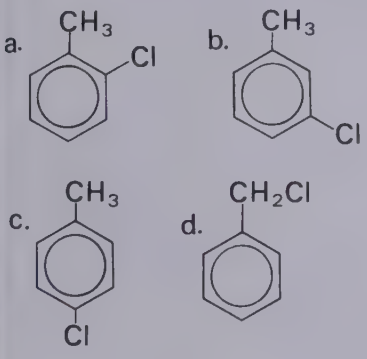
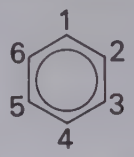
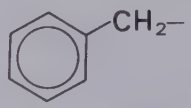



*Figure 11. Structural isomers of $C_7H_7Cl$*

The first three isomers are named by numbering the benzene ring from 1 to 6. In the case of benzene itself all six hydrogens are




identical and so in the case of a substituted benzene the 2 and 6, and 3 and 5 positions are identical. The convention used is to take the positions which give the smallest numbers, e.g. 1, 2 not 1, 6; 1, 3 not 1, 5. The fourth isomer contains the group:




which is called the benzyl group, hence the name benzyl chloride.

Another possible type of isomerism can occur if the *aliphatic unsaturated* compounds are considered. Whereas a single bond can rotate freely in space, it is not possible for rotation to take place about a multiple bond. This leads to the existence of **geometric isomers**.

Geometric isomers contain the same numbers of each kind of atom and do not differ in regard to which atom is linked to which. They do differ in the way in which the atoms are arranged in space. Consider the compound with molecular formula $C_2H_2Cl_2$. This is an unsaturated aliphatic compound, called 1, 2-dichloroethene, and the two possible geometric isomers are shown in figure 12.

The isomer with like groups on the same side of the double bond is called the cis isomer, and the other, with the groups on opposite sides of the double bond is called the trans isomer.

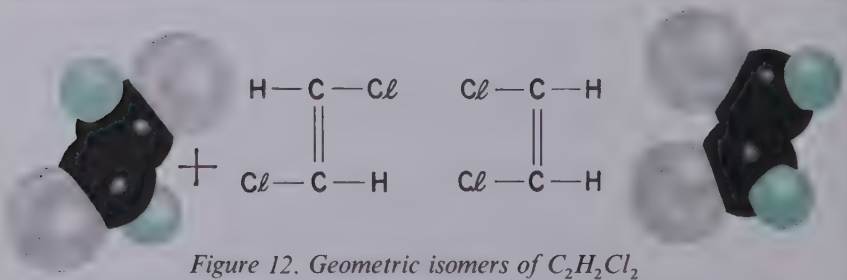



*Figure 12. Geometric isomers of $C_2H_2Cl_2$*

There is usually little, or no, difference in the chemical properties of such isomers but they have very different physical properties (table 3). This last point is useful in their separation.

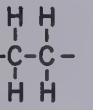
*Table 3. Physical properties of the geometric isomers of 1, 2-dichloroethene*

| COMPOUND | MOLECULAR FORMULA | ISOMER | MELTING POINT | BOILING POINT |
|---|---|---|---|---|
| 1, 2-dichloroethene | $C_2H_2Cl_2$ | cis | -82°C | 60°C |
| | | trans | -49°C | 48°C |

## Functional Groups and Nomenclature

So far several different organic compounds have been discussed, and the names simply given without any reference as to how those names have been derived. We shall describe the system of nomenclature in this section.

Earlier, in structural determination, the properties of ethanol were explained on the basis that the compound contained an oxygen atom linked to a hydrogen atom, that is, the molecule contains an —OH group. In most of the reactions of ethanol the remainder of the molecule remains unchanged. Ethanol can be considered as being made up of two parts:


and —O—H or $CH_3CH_2$— and —OH

These are known as **functional groups** because it is such groups which are responsible for the type of chemical reaction shown by a particular class of compounds.

The $\mathbf{C_2H_5}-$ or *ethyl* group usually remains unchanged in the reactions of ethanol whereas the **—OH** or *hydroxyl* group is very reactive.

The ethyl group can be thought of as being derived from the parent hydrocarbon, ethane, $C_2H_6$. Ethane is one member of a series of saturated hydrocarbons called the **alkanes.** The first ten members of this series are shown in table 4.

*Table 4. Names and molecular formulas of the first ten members of the alkane series of hydrocarbons*

| NAME | MOLECULAR FORMULA |
|---|---|
| methane | $CH_4$ |
| ethane | $C_2H_6$ |
| propane | $C_3H_8$ |
| butane | $C_4H_{10}$ |
| pentane | $C_5H_{12}$ |
| hexane | $C_6H_{14}$ |
| heptane | $C_7H_{16}$ |
| octane | $C_8H_{18}$ |
| nonane | $C_9H_{20}$ |
| decane | $C_{10}H_{22}$ |

Just as the *ethyl* group can be thought of as being derived from *ethane*, other groups can be derived from the rest of the alkanes, for example

$\mathbf{CH_3}-$ *methyl* from methane
$\mathbf{C_3H_7}-$ *propyl* from propane
$\mathbf{C_4H_9}-$ *butyl* from butane, and so on.

This family of groups, derived from the alkanes, is called the *alkyl* series and is one example of a series of functional groups. If the chemistry of a particular functional group is known for one compound, it is a fair assumption that the chemistry of other compounds containing that same functional group will be closely

related. We shall find the knowledge of functional groups one of the most useful concepts in the study of carbon compounds.

Thus all compounds which contain the **—OH** group are called *alkanols* or *alcohols* and have similar chemical reactions because of that group. The name of the alcohol is worked out from the alkyl group it contains.

**Example**

$CH_3OH$ is methanol or methyl alcohol
$C_2H_5OH$ is ethanol or ethyl alcohol
$C_6H_{13}OH$ is hexanol or hexyl alcohol

It is very important to realize that these functional groups are simply parts of molecules. They cannot be isolated as such. A list of common functional groups is given in table 5.

The increasing number, and complexity, of carbon compounds eventually forced chemists to consider a systematic scheme of nomenclature. Such a system enables complex molecules to be fairly readily recognized and their structures to be worked out. The present scheme is universally accepted.

## System used for Naming the Various Types of Compounds

### (1) Alkanes

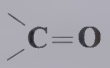
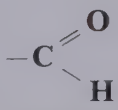
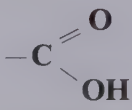
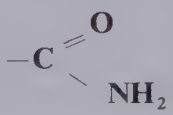
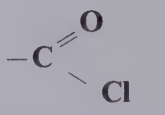
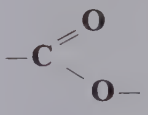
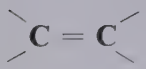
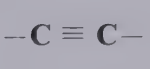
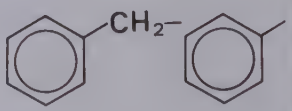
Saturated aliphatic alkanes are named as follows:

$C_1$—methane $C_2$—ethane $C_3$—propane $C_4$—butane
$C_5$—pentane $C_6$—hexane $C_7$—heptane $C_8$—octane
$C_9$—nonane $C_{10}$—decane

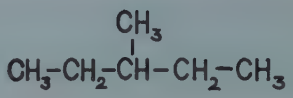
### (2) Branched alkanes

(a) Find the longest chain (or one of the longest chains).
(b) Consider the remainder as functional groups and name them by changing *-ane* to *-yl*, e.g. propane becomes propyl, etc.
(c) Number the longest chain from one end to the other and use the numbers as locants to describe the positions of the functional groups.

*Table 5. Names and formulas of common functional groups*

| | | | | | |
|---|---|---|---|---|---|
| $CH_3-$ methyl | $C_2H_5-$ ethyl | $C_3H_7-$ propyl | $C_4H_9-$ butyl | $C_5H_{11}-$ pentyl | $C_6H_{13}-$ hexyl |
| $C_7H_{15}-$ heptyl | $C_8H_{17}-$ octyl | $-Cl$ chloride | $-Br$ bromide | $-I$ iodide | $-OH$ hydroxyl (alcohol) |
|  carbonyl (ketone) |  aldehyde |  carboxyl (acid) | $-O-$ ether | $-NO_2$ nitro | |
| $-NH_2$ amine |  amide |  acid chloride |  ester | | |
|  alkene |  alkyne | acid anhydride |  benzyl | phenyl | |

**Example**

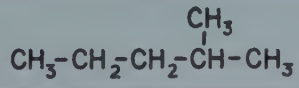


The longest chain contains five carbon atoms so the compound is a substituted pentane.

Substituting group is $CH_3$ so is named methyl.
It is located on third carbon atom.
∴ compound is 3-methyl pentane.

REMEMBER: *Start numbering from the end that will give the smaller number.*

**Example**

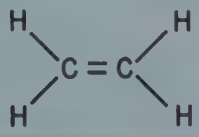


is 2-methyl pentane *not* 4-methyl pentane

**(3) Unsaturated Aliphatic Hydrocarbons**

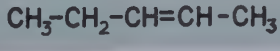
**(a)** The suffix *-ene* is used to denote one carbon-carbon *double* bond. If two carbon-carbon double bonds are present, the suffix used is *-diene*, etc. The rest of the name is derived from the number of carbon atoms present and the locant is the smaller of the two numbers referring to the two carbon atoms between which the double bond is located.

**Example**



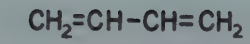
This compound contains one carbon-carbon double bond so the suffix is *-ene*. There are two carbon atoms in the molecule so the compound must be ethene.

**Example**

 pent-2-ene

Again number from the end that will afford the smaller locant.

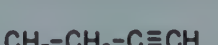
**Example**



This compound contains two carbon-carbon double bonds so the suffix is *-diene*. There are four carbon atoms in the molecule so the compound is butadiene. The double bonds are between the first and second and third and fourth carbon atoms so the compound is called buta-1, 3-diene.

**(b)** The suffix *-yne* is used to denote one carbon-carbon triple bond.

**Example**



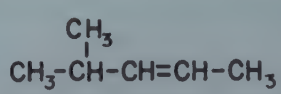
This compound contains one carbon-carbon triple bond, so the suffix is *-yne*. There are four carbon atoms in the molecule so the compound is butyne. The multiple bond is between the first and second carbon atoms so the compound is called but-1-yne.

**Example**

but-2-yne

**(c)** If the unsaturated hydrocarbon is branched, the system used is the same as for branched alkanes.

**Example**



The longest chain contains five carbon atoms and has one carbon-carbon double bond, so the substance is a substituted pentene. The double bond is between the second and third carbon atoms so the substance is a substituted 2-pentene. The

substituting group is $CH_3-$ and located on the fourth carbon atom, so the complete name is 4-methyl pent-2-ene.

### (4) Derivatives of Benzene

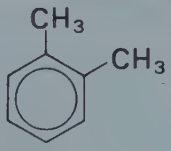
These are best named as *benzenes*, but some traditional names are still used.

**Example**

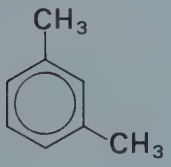
methyl benzene or toluene

With *two or more* substituting groups on the benzene ring the numbering system is used to distinguish between isomers.

**Examples**



1, 2 dimethyl benzene



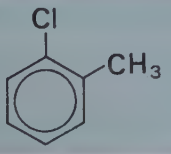
1, 3 dimethyl benzene

1, 4 dimethyl benzene

**With different substituents, the substituents must be listed alphabetically.**

This is a general rule and applies in all cases.

**Example**



1-chloro-2-methyl benzene *not* 1-methyl-2-chlorobenzene.

**(5) Halides**

These are named from the appropriate hydrocarbon with prefixes: *fluoro*, *chloro*, *bromo*, *iodo*,
*or* from the appropriate alkyl radicals followed by the suffixes: *fluoride*, *chloride*, *bromide*, *iodide*.

**Example**

$CH_3CH_2CH_2I$ is 1-iodopropane or 1-propyl iodide,
Either system is acceptable.

**(6) Alkanols or alcohols**

These are denoted by prefix *hydroxy* or suffix *-ol*, preceded by the locant.

**Example**

$CH_3CH_2CHOHCH_3$ is 2-hydroxybutane or 2-butanol because there are four carbon atoms in the molecule and the hydroxyl group is attached to the second carbon atom.

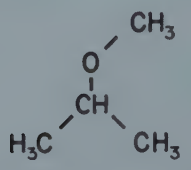
**(7) Ethers**

These have oxygen bound to two carbon atoms. They are named as follows:

**(a)** choose the longer radical to supply the name of the frame, and

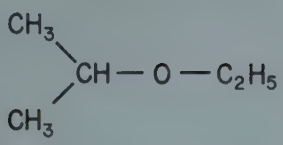
**(b)** name the remainder methoxy ($CH_3O$—), ethoxy ($C_2H_5O$—), propoxy ($C_3H_7O$—), etc.

**Example**




The longer of the two alkyl radicals contains three carbon atoms, so the substance is a derivative of propane.
—propane group is branched so must be 2..... propane.
—remainder is $CH_3O$— so full name is 2-methoxypropane.
An alternative system is simply to name the two alkyl radicals.

**Example**

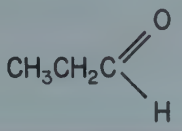


is 2-ethoxypropane on the system above, or ethyl 2-propyl ether on the alternative system, since these are the alkyl radicals joined to the oxygen.

**(8) Alkanals or aldehydes**

They are named by the suffix *-al.*

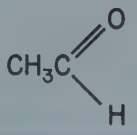
**Example**



propanal

In the first case all three carbon atoms are considered together.

**Example**

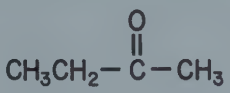


ethanal

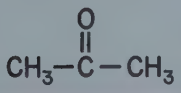
**(9) Alkanones or ketones**

They are named by the suffix *-one.*

**Examples**



butanone



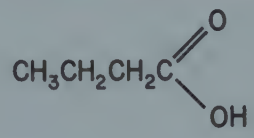
propanone

The last compound is still likely to retain its better known name of acetone.

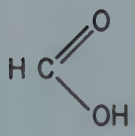
### (10) Carboxylic acids

They are denoted by the suffix *-oic acid.*

**Examples**

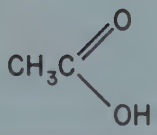


1-butanoic acid



methanoic acid

There is no need to use the locant with methanoic acid because it only contains one carbon atom. Its better known name is formic acid.



ethanoic acid

Its better known name is acetic acid.

### (11) Amines

These are named from the appropriate hydrocarbon, with the prefix *amino*
*or* from the appropriate alkyl radical followed by the suffix *amine*

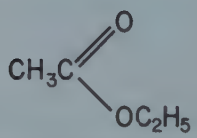
**Example** $CH_3CH_2NH_2$ amino ethane *or* ethyl amine

### (12) Derivatives of Carboxylic Acids

(a) *Esters*—designate as *-oate* preceded by the appropriate alkyl radical.

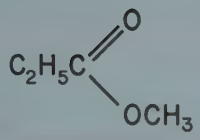
**Example**

ethyl ethanoate



is so named because the alkyl radical contains two carbon atoms and so does the carboxylic acid group.

**Example**



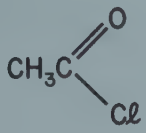
methyl propanoate

**Exercise 3**

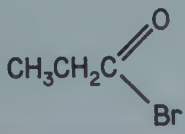
These last two compounds are not the same. Why is this so and what name would you give to the property causing the difference?

(b) *Acid Halides*—designate as *-oyl*, followed by the appropriate halide radical.

**Examples**



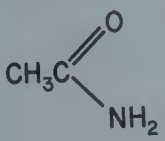
ethanoyl chloride



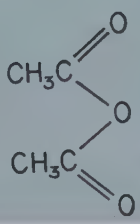
propanoyl bromide

(c) *Amides and Acid Anhydrides*—best named from the corresponding acid.

**Examples**



ethanamide



ethanoic anhydride, also called acetic anhydride.

REMEMBER: *Certain names in common usage, although not acceptable on the system of terminology accepted by international agreement, will still be retained.*

For example $C_2H_2$ will still be called **acetylene** instead of the name **ethyne.** (Imagine oxy-ethyne welding as a common phase!) $CH_3COOH$ is still likely to be called acetic acid instead of ethanoic acid, and so on.

Practice in this system of nomenclature will soon enable you to work out names from formulas and vice versa. A representative set of examples is included in the revision questions at the end of the text.

## The Chemistry of Some Typical Functional Groups

At first glance organic chemistry may seem to be a mass of unrelated reactions, but closer examination shows that there are, in fact, very few different reactions. To appreciate this you must familiarize yourselves with two important concepts. First, the reactions of a particular functional group show only slight variation, usually in speed and ease of reaction, no matter what compound it appears in; and secondly, we must consider a *homologous series.*

### Homologous Series

Consider the alkyl iodides:

| | | |
|---|---|---|
| $CH_3I$ | iodomethane | or methyl iodide |
| $C_2H_5I$ | iodoethane | or ethyl iodide |
| $C_3H_7I$ | iodopropane | or propyl iodide |
| $C_4H_9I$ | iodobutane | or butyl iodide, etc. |

Besides the carbon atom, which is added with each succeeding molecule, two hydrogen atoms are added. Thus, in passing from

one molecule to the next, we can see that each succeeding molecule increases by the common increment $-\mathbf{CH_2}$. This is an example of a **homologous series,** and the individual members of each series are called *homologues*.

There are many of these *homologous series* to be found in organic chemistry and each has the following properties in common:

(1) All members of a particular series can be represented by a general molecular formula, and each member of the series differs from the next by $-\mathbf{CH_2}$.
For example, the alkyl iodides have general group formula $\mathbf{C_nH_{2n+1}I}$.

**Exercise 4**

What is the general group formula of:
(**a**) the alkanes?
(**b**) the alkanols?

(2) The *physical properties* of the members of a homologous series show a gradual, but regular, change as the series is ascended, i.e. as the molecular formula becomes more complex. For example, boiling points and melting points steadily increase.
(3) All members of a particular series exhibit the same general *chemical properties*, although reaction becomes more difficult as the molecule becomes more complex.

This last property is the most important one. It means that once a student has acquired a sound knowledge of the preparation and reactions of a typical member of a homologous series, he knows the chemistry of *all* the members in that series. Exceptions do appear, but the above statement is on the whole a true one.

## A Sequence of Reactions using Methyl Iodide

### (1) Conversion of the Iodide Group to the Hydroxyl Group

If methyl iodide is heated with aqueous sodium hydroxide, reaction takes place to give methanol.

$$CH_3I_{(l)} + OH^-_{(aq)} = CH_3OH_{(l)} + I^-_{(aq)}$$

Only poor yields of methanol are obtained, and a better method is to stir the methyl iodide with a suspension of silver oxide in moist ether (diethyl ether). This latter reagent *in effect* provides 'silver hydroxide' and the following reaction takes place.

$$CH_3I_{(l)} + AgOH_{(s)} = CH_3OH_{(l)} + AgI_{(s)}$$

Because the reaction involves bonds which are predominantly covalent, it takes far longer than an ionic reaction. If sodium hydroxide is used, the best results are obtained using a concentrated solution at high temperatures.

Why is this reaction different from the reaction between hydriodic acid and sodium hydroxide? Experimental investigation reveals the following facts:

(a) The bonds in methyl iodide are predominantly covalent as shown by its low boiling point, poor solubility in water, and the fact that the solution does not conduct electricity, showing that no ions are formed.

(b) The reaction takes longer to carry out than the reaction between hydriodic acid and sodium hydroxide which is instantaneous.

(c) By carrying out the reaction under varying conditions, it can be shown that better yields are obtained (and obtained at a quicker rate) using concentrated sodium hydroxide at high temperatures.

With these results, chemists have been able to suggest a possible mechanism for the reaction. The reaction scheme suggests three stages:

(i) the approach of the hydroxide ion to the covalent methyl iodide,
(ii) formation of an activated complex, and
(iii) formation of the final products.

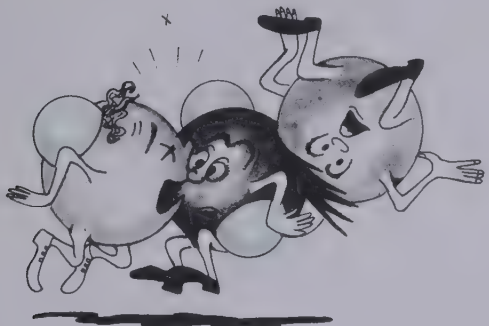
This type of activated complex is an accepted theory in reaction mechanisms and it is considered that the formation of a new bond (in this case **O—C**) and the breaking of an old bond (in this case **C—Br**) are occurring simultaneously.

We can picture this as follows:

**(a)** approach of reactants

(a) $OH^-_{(aq)}$ + $CH_3I_{(l)}$

**(b)** formation of activated complex



(b) $OH.....CH_3.....I$

**(c)** formation of products

(c) $CH_3OH_{(l)}$ + $I^-_{(aq)}$

The mechanism is entirely different from the neutralization reaction taking place between hydriodic acid and sodium hydroxide.

$$HO^-_{(aq)} + H_3O^+_{(aq)} = 2H_2O_{(l)}$$

### (2) Conversion of the Hydroxyl Group to the Aldehyde Group

Once formed, the methanol can react further. Like all primary alcohols it can be oxidized by common inorganic oxidizing agents. One of the best of these oxidising agents is acidified potassium dichromate.

When reaction takes place, the colour of the solution changes from orange to green due to formation of chromium (III) ions. The half reaction for the reduction of the dichromate ion is:

$$Cr_2O_{7(aq)}^{2-} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$

The methanol is converted to methanal (an aldehyde).

$$CH_3OH \rightarrow H-C\begin{matrix}=O\\ \diagdown H\end{matrix} + 2H^+_{(aq)} + 2e^-$$

The two half reactions are then balanced in terms of electrons and added together:

$$Cr_2O_{7(aq)}^{2-} + 8H^+_{(aq)} + 3CH_3OH_{(l)} = 2Cr^{3+}_{(aq)} + 7H_2O_{(l)} + 3HC\begin{matrix}=O\\ \diagdown H\end{matrix}$$

### (3) Conversion of the Aldehyde Group to the Carboxyl (Acid) Group

The methanal represents one stage in the oxidation of methanol. Further oxidation can be brought about by treating methanol with acidified potassium permanganate.

The half reaction for the permanganate is:

$$MnO^-_{4(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$$

and the methanol is converted to methanoic acid.

$$CH_3OH_{(l)} + H_2O_{(l)} \rightarrow HC\begin{matrix}=O\\ \diagdown OH\end{matrix} + 4H^+_{(aq)} + 4e^-$$

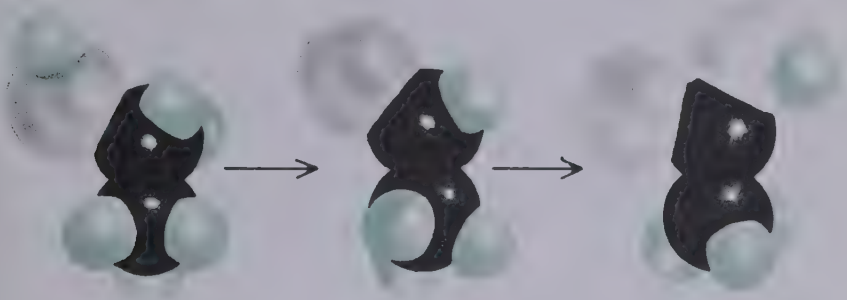
Again balancing the electrons and adding together:

$$4MnO_{4(aq)}^{-} + 12H_{(aq)}^{+} + 5CH_3OH_{(l)} = 4Mn_{(aq)}^{2+} + 11H_2O_{(l)} + 5HC(=O)OH$$

### (4) Oxidation of the Carboxyl (Acid Group)

Complete oxidation, can be brought about by combustion of the methanoic acid with oxygen. As with *all* organic compounds, the products of complete oxidation are carbon dioxide and steam.

Just as methanol could be oxidized in two stages, ethanol can also be oxidized in two stages. In this case the products are ethanal and ethanoic acid.



$$C_2H_5OH \longrightarrow CH_3-C(=O)H \longrightarrow CH_3-C(=O)OH$$

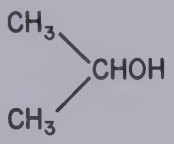
**Exercise 5**

Work out the balanced equations for the oxidation of ethanol to:
(**a**) ethanal, using acidified dichromate solution, and
(**b**) ethanoic acid, using acidified permanganate solution.

With propanol, two routes are possible because there are two isomers of propanol. We can use the rules of valence to draw up graphic formula for the two isomers. They are:

**$CH_3CH_2CH_2OH$**
1-propanol

and



2 propanol

1-propanol is classified as a *primary* alcohol because it contains the —**$CH_2OH$** group,
2-propanol is a *secondary* alcohol because it contains the

$\gtrless$**CHOH** groups,

and a third classification is a *tertiary* alcohol which contains the

$\gtrless$**COH** group.

**Examples**

| | |
|---|---|
| $CH_3CH_2CH_2CH_2OH$ | 1-butanol (a primary alcohol) |
| $CH_3CH(CH_2OH)CH_3$ | 2-methyl propanol or *iso*butanol (also a primary alcohol) |
| $CH_3CH_2CH(OH)CH_3$ | 2-butanol (a secondary alcohol) |
| $(CH_3)_3C(OH)CH_3$ | *tert* -butanol (a tertiary alcohol) |

1-propanol, the primary alcohol, is **$CH_3CH_2CH_2OH$**. Oxidation will give propanal and propanoic acid.

$$CH_3CH_2CH_2CHOH \longrightarrow CH_3CH_2C(=O)H \longrightarrow CH_3CH_2C(=O)OH$$

2-propanol, the secondary alcohol, is $(CH_3)_2CHOH$

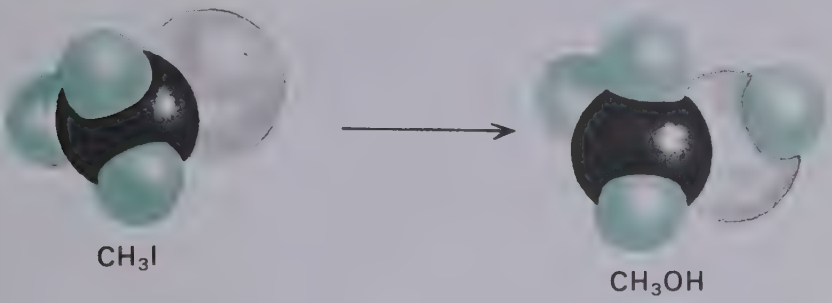
The product of oxidation in this case is an *alkanone* or *ketone* called propanone (the older name for this compound is acetone).

$$(CH_3)_2CHOH \longrightarrow (CH_3)_2C=O$$

The alkanones or ketones cannot be oxidized to acids, but complete combustion with oxygen will, as always, give carbon dioxide and steam.

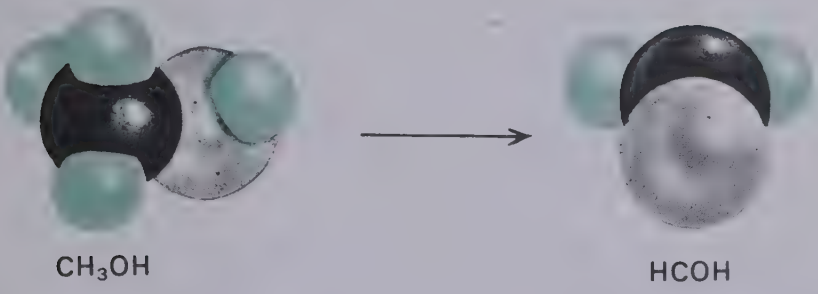
Returning to methyl iodide, consider the sequence of reactions from a structural point of view.

**(a)** Methyl iodide is converted to methanol.



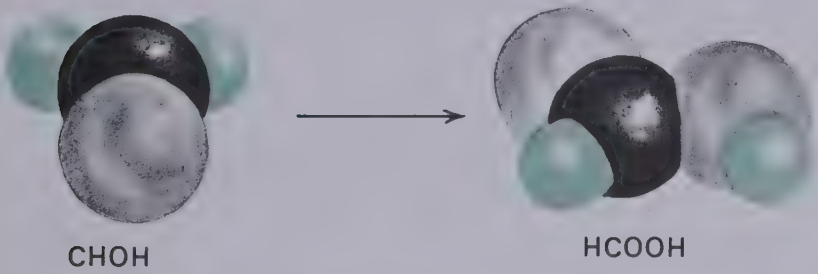

This is a substitution reaction.

**(b)** Methanol is converted to methanal.



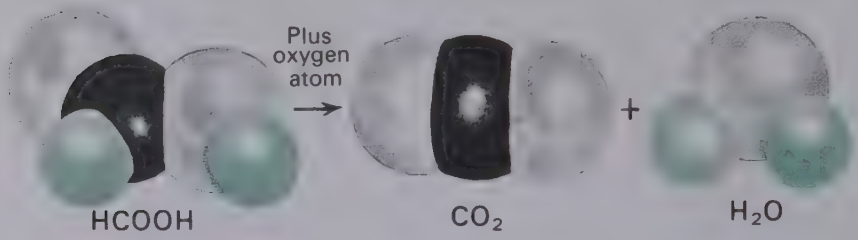

This is oxidation, resulting in removal of two hydrogen atoms.

**(c)** Methanal is converted to methanoic acid.

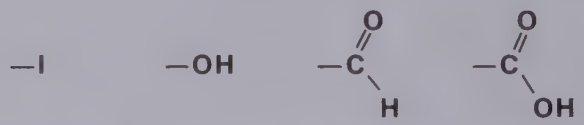



Again this is oxidation, this time resulting in the addition of an oxygen atom.

(**d**) Methanoic acid is converted to carbon dioxide and steam.




Once again this is oxidation, resulting in addition of an oxygen atom. So far we have studied four typical functional groups:




It is groups such as these which give the different members of the respective homologous series their characteristic chemical properties. One way of focusing attention on the functional group is to use the general symbol **R**—, to represent that part of the molecule that does not change. In most cases, therefore, **R**— will represent an alkyl group.

**Example**

$$\mathbf{R}CH_2I + OH^-_{(aq)} = \mathbf{R}CH_2OH + I^-_{(aq)}$$

$$3\mathbf{R}CH_2OH + Cr_2O_{7(aq)}^{2-} + 8H^+_{(aq)} = 3\mathbf{R}C(=O)H + 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$

$$3\mathbf{R}C(=O)H + Cr_2O_{7(aq)}^{2-} + 8H^+_{(aq)} = 3\mathbf{R}C(=O)OH + 2Cr^{3+}_{(aq)} + 4H_2O_{(l)}$$

You will meet more of these functional groups as you study the different homologous series, and it is most important to remember that *the properties of a particular group remain little altered regardless of the group to which it is attached.*

# Hydrocarbons

A *hydrocarbon* is a substance that contains *carbon and hydrogen only*. This must not be confused with a *carbohydrate* which is one class of substance containing carbon, hydrogen and oxygen.

Hydrocarbons can be either **saturated** (have only single carbon-carbon bonds in the molecule), or **unsaturated** (contain multiple carbon-carbon bonds). They can be further subdivided into distinct homologous series. The four main homologous series of hydrocarbons are:

- THE ALKANES,
- THE ALKENES,
- THE ALKYNES, and
- THE BENZENES

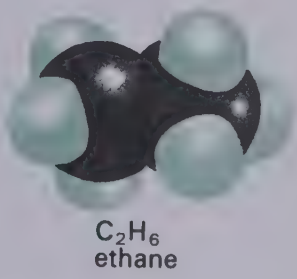



*Figure 13. Three-dimensional representation of ethane*

## The Alkanes

The alkanes are a homologous series of **saturated** hydrocarbons of general formula $\mathbf{C_nH_{2n+2}}$. The names and formulas of the first eight members are given in table 4 (page 28).

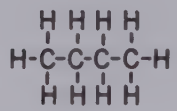
Like all homologous series there is a definite but regular gradation in physical properties (see table 6).

As the molecule becomes more complex, melting points and boiling points steadily increase. Thus the lower members are gases at normal temperatures, changing to liquids, and finally, after $C_{16}H_{34}$ (hexadecane) to waxy solids.

The lower members of the series are sparingly soluble in water but more soluble in ethanol, and the higher members are insoluble in both these, and most other solvents. All the alkanes are less dense than water. The alkanes are characterized by inertness to

chemical reactions, being unaffected by such reagents as hot nitric acid, hot caustic alkalis, and strong oxidizing agents. The few chemical reactions they undergo include halogenation, nitration and combustion. It is this latter reaction that makes the alkanes, and other hydrocarbons, such an important energy source, and in fact the main source of the alkanes is as a complicated mixture in crude petroleum.

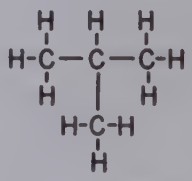
Isomerism first occurs in the alkane series with butane, which can exist in two isomeric forms.

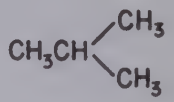


$CH_3CH_2CH_2CH_3$

*n*-butane

and





2-methyl propane

The number of theoretically possible structures rises rapidly as the molecule becomes more complex.

*Table 6. Physical properties of some alkanes*

| NAME | STRUCTURAL FORMULA | DENSITY (Kg/litre) | MELTING POINT (°C) | BOILING POINT (°C) | HEAT OF COMBUSTION (Kcal/mole) |
|---|---|---|---|---|---|
| methane | $CH_4$ | 0.415 | −182 | −162 | 213 |
| ethane | $CH_3CH_3$ | 0.572 | −183 | −89 | 373 |
| propane | $CH_3CH_2CH_3$ | 0.585 | −188 | −42 | 531 |
| *n*-butane | $CH_3CH_2CH_2CH_3$ | 0.601 | −138 | −0.5 | 688 |
| 2-methyl propane | $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{CH}}}}-CH_3$ | — | −159 | −12 | 686 |
| *n*-hexane | $CH_3CH_2CH_2CH_2CH_2CH_3$ | 0.659 | −95 | +69 | 1003 |

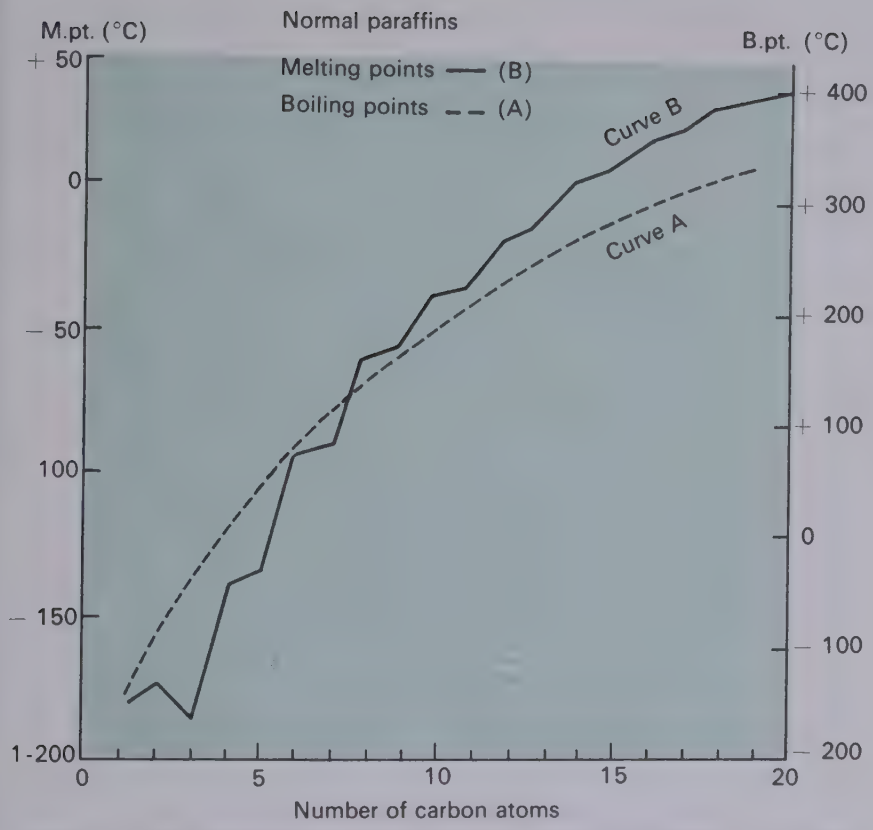



*Figure 14. Graph showing variations of melting point and boiling point of the alkane hydrocarbons with increase in molecular complexity*

## The Alkenes

The alkenes are a homologous series of **unsaturated** hydrocarbons. They contain **one carbon-carbon double bond** and have general group formula $\mathbf{C_nH_{2n}}$. Theoretically the first member of the series would be $CH_2$ (methene) but this only exists as a free radical in certain chemical reactions, i.e. it is incapable of independent existence. The simpler members of the series are shown in table 7. The alkenes resemble the alkanes in *physical* properties. The lowest members of the series are gases ($C_2$ to $C_4$), then liquids ($C_5$ to $C_{15}$), and finally solids. The gases are somewhat soluble in water but the liquids and solids are not. Melting points and boiling points increase as the molecules become more complex. All the members of the series are colourless and inflammable, burning with a luminous flame to form carbon dioxide and water.

*Table 7. Names and molecular formulas of the first seven members of the alkenes*

| NAME | MOLECULAR FORMULA |
|---|---|
| ethene | $C_2H_4$ |
| propene | $C_3H_6$ |
| butene | $C_4H_8$ |
| pentene | $C_5H_{10}$ |
| hexene | $C_6H_{12}$ |
| heptene | $C_7H_{14}$ |
| octene | $C_8H_{16}$ |

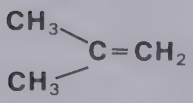
In contrast to the alkanes, the alkenes are chemically reactive. This reactivity is associated with the carbon-carbon double bond which is a source of 'weakness' in the molecule.

Most of the reactions are classified as **addition** reactions, whereby one of the bonds of the double bond opens and a new atom becomes bonded to each of the carbon atoms. These and other chemical reactions of the hydrocarbons will be considered in the NSCM Booklet C14 *The Chemistry of Carbon—Part II.*

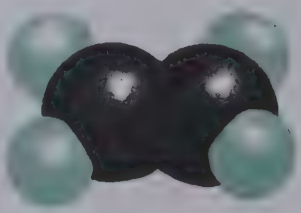
Isomerism first occurs with butene which exists in three isomeric forms:

$CH_2=CH-CH_2-CH_3$ but-1-ene

$CH_3-CH=CH-CH_3$ but-2-ene (can exist in *cis* and *trans* form)



2-methylpropene or *iso*-butene



$C_2H_4$
ethene

*Figure 15. Three-dimensional representation of ethene*

It must be noted that there are more isomers in the alkene series than in the alkane series, because of additional isomerism due to:

**(a)** different locations of the carbon-carbon double bond, and
**(b)** *cis* and *trans* configurations at that double bond.

### The Alkynes

The alkynes are a homologous series of **unsaturated** hydrocarbons. They contain **one carbon-carbon triple bond** and have general group formula $\mathbf{C_nH_{2n-2}}$. The simpler members of the series are shown in table 8.

*Table 8. Names and molecular formulas of some of the alkynes*

| NAME | MOLECULAR FORMULA |
|---|---|
| ethyne (acetylene) | $C_2H_2$ |
| propyne | $C_3H_4$ |
| butyne | $C_4H_6$ |
| pentyne | $C_5H_8$ |

Again there is similarity in physical properties to both the alkanes and alkenes. The series starts with three gases ($C_2$ to $C_4$), followed by liquids, and finally solids. The alkynes are colourless and sparingly soluble in water. They burn with a luminous flame and can form explosive mixtures with air or oxygen.

Chemically they are even more reactive than the alkenes because of the carbon-carbon triple bond. Characteristic chemical reactions involve addition across this multiple bond, the first product of the reaction being a derivative of an alkene which then undergoes further addition.

$C_2H_2$
acetylene

*Figure 16. Three-dimensional representation of ethyne (acetylene)*

Isomerism first occurs with butyne which exists in two isomeric forms:

$CH_3-CH_2-C\equiv CH$ but-1-yne

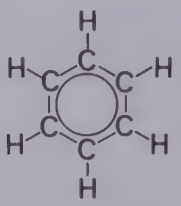
$CH_3-C\equiv C-CH_3$ but-2-yne

The alkynes do not exhibit *cis—trans* isomerism. This is because the carbon valence bonds at the extremities of the triple bond are collinear.

**The Benzenes**

The benzene hydrocarbons are a homologous series of **unsaturated aromatic cyclic** compounds. We saw earlier that aromatic compounds contain rings of carbon atoms, and in fact all such compounds are considered derived from benzene. The first member of the series is benzene itself which has a molecular formula $\mathbf{C_6H_6}$. The benzene ring is planar with 120° angles between each pair of bonds formed by a given carbon atom.

The molecule is thus a regular hexagon.

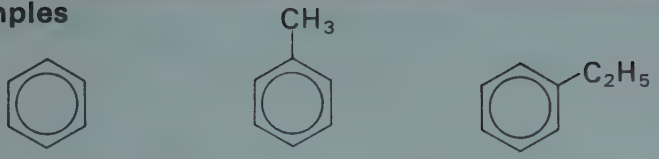


All six carbon-carbon bonds are identical so the structural formula is usually expressed as:

to satisfy the valence of carbon, i.e. the carbon-carbon double bonds are *delocalized*, or shared with the whole of the molecule.

The other members of the homologous series are derived from benzene by replacing one, or more, of the six equivalent hydrogen atoms by alkyl groups.

**Examples**




benzene methyl benzene ethyl benzene

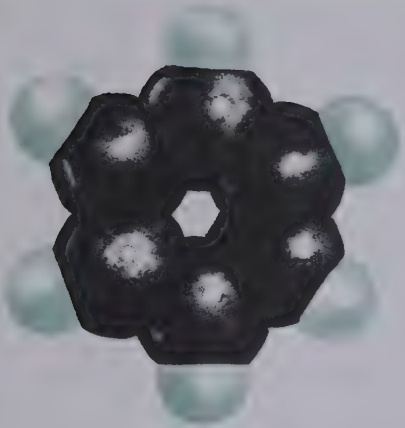
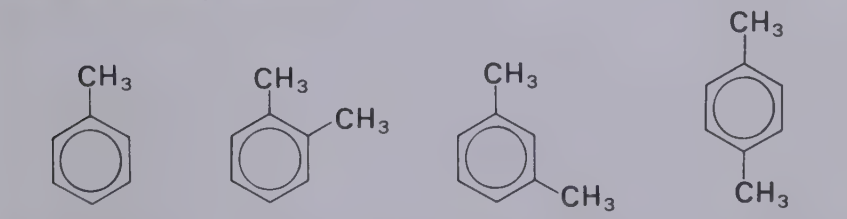


*Figure 17. Three-dimensional representation of benzene*

The benzenes are all colourless liquids which are sparingly soluble in water, and less dense than water. They are inflammable and burn with a luminous flame. Most of the members of the series, and in particular benzene itself, are extremely *toxic* and care should be taken that the vapours are not inhaled.

The benzenes show neither the typical reactivity, nor the usual addition reactions of the alkenes. In most reactions the multiple bond structure is not affected because of its **delocalization,** and the characteristic reaction of benzene, and its homologues, is substitution.

Isomerism first occurs with ethyl benzene which is isomeric with the dimethyl benzenes.




ethyl benzene 1, 2 dimethyl benzene 1, 3 dimethyl benzene 1, 4 dimethyl benzene

Chemical reactions of the various homologous series will be studied in the NSCM Booklet C14 *The Chemistry of Carbon—Part II.*

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## Revision Questions

**1** An organic compound was allowed to react with hot metallic sodium. The product was allowed to dissolve in water; some hydrogen was evolved in the process. Silver nitrate was added and a dark precipitate formed. A portion of the suspension was treated with dilute nitric acid and the solution became clear. To another portion of the suspension, dilute hydrochloric acid was added and the precipitate became white, while a gas evolved which turned potassium dichromate paper green; also a smell of hydrogen sulphide was observed.

Which of the following do you consider reasonable deductions from the foregoing observations?

(a) The organic compound was an acid.
(b) The organic compound contained chlorine.
(c) Sulphur in the compound formed sodium sulphate on reacting with sodium.
(d) The organic compound contained oxygen.
(e) Sodium was used in excess of the amount required to react with the organic compound.

In each case briefly state your reasons for considering the statement *true* or *false*.

**2** Calculate the empirical formula of the silver salt of a monobasic organic acid which contains 26.01% carbon, 2.91% hydrogen, 20.58% fluorine and 38.95% silver.

**3** A substance contains 16.3% carbon, 0.68% hydrogen and 72.16% chlorine. Calculate the empirical formula.

**4** Combustion of 0.232g of a compound X gave 0.2003g carbon dioxide and 0.0687g water. X also contains 52.34% bromine. Find the empirical formula of X. If the molecular weight of X does not exceed 200, write a structural formula that satisfies the rules of valence.

**5** 1.24g of an organic compound Y, which contains carbon, hydrogen and oxygen only, gives 2.73g carbon dioxide and 1.49g water on complete combustion. Calculate the empirical formula of the compound Y. If the molecular formula of Y is the same as the empirical formula, write possible structural formulas for the compound.

**6** Outline the plan of action generally followed in order to elucidate the structure of an organic compound. Describe in detail the theory and practice of the Lassaigne sodium fusion test.

**7** Explain clearly what is meant by *isomerism*. Give the structure of all the isomeric hydrocarbons corresponding to (a) $\mathbf{C_5H_{12}}$ (b) $\mathbf{C_4H_8}$.

**8** Draw the structure of all possible compounds called trihydroxy benzene.

**9** What do you understand by the term 'functional group'? Give *one* example of such a group containing:
(a) nitrogen;
(b) oxygen; and
(c) nitrogen and oxygen.

**10** Name the following carbon compounds:

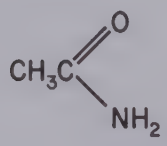
$CH_3CH_2CH(CH_3)CH_3$ $CH_3CH(C_2H_5)CH_2CH_2CH_3$

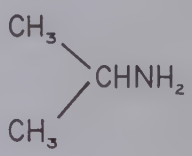
$CH_2{=}CH{-}CH{=}CH{-}CH_3$

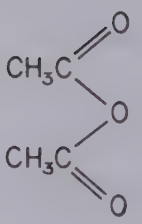
$CH_3CH{=}CHCH_3$ $CH_3CH_2{-}CH{=}CH_2$

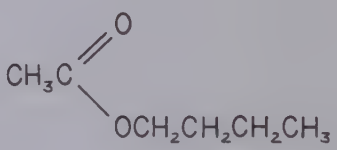
$CH_3CH_2CH_2I$ $CCl_4$

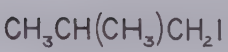
**11** Name the following carbon compounds:

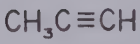


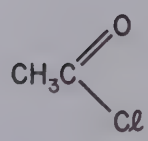












**12** Write structural formulas for:
ethyl methanoate, *tert*-butanol, benzyl alcohol, 2-methoxy propane, propanal, propanone, butanoic acid, methyl ethanoate.

**13** Write structural formulas for:
methanol, ethene, ethyl ethanoate, 1-bromo-3-aminobenzene, iodopropane, ethanoyl chloride, ethanal, 2-methylpentane.

**14** What are the characteristics of a homologous series? Illustrate your answer with well-chosen examples.

**15** Give the general group formula for the following homologous series (a) the alkanes, (b) the alkenes, (c) the alkynes, (d) the benzenes. Explain the difference between saturated and unsaturated compounds. How would you test for unsaturation in a carbon compound?

**16** Allot the following compounds to their respective series of hydrocarbons:

$C_{12}H_{26}$ $C_9H_{16}$ $C_7H_{14}$ $C_{32}H_{62}$ $C_{12}H_{18}$ $C_5H_{10}$
$C_8H_{10}$ $C_6H_{12}$ $C_{20}H_{42}$ $C_{15}H_{28}$ $C_{20}H_{34}$

**17** Define a hydrocarbon. How does it differ from a carbohydrate? Describe what happens when sugar is strongly heated in the absence of air. What does this tell you about the chemical composition of sugar?

**18** Give two examples of hydrocarbons in everyday use, stating their use, and giving the names and structural formulas.

**19** How many products can be obtained from a reaction between chlorine and methane? Give the name and structural formulas of these products?

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Peter Calcraft was born in Skegness (U.K.), a small seaside town, but moved to the industrial Midlands at a very early age. He matriculated at Long Eaton Grammar School and left there to become a laboratory assistant in the Organic Research Department of Boots (Nottingham). As a result of part-time study whilst still employed at Boots, he gained an Honours degree in Chemistry from London University. Half way towards completing a Ph.D. in heterocyclic systems, the Japanese published work of a too similar nature. This nine years' organic research experience, finally as a senior technician, led to a love of this topic which still persists.

Mr Calcraft entered the teaching profession in 1958 and, after experience at Heanor and Mundella Grammar Schools, became Head of the Chemistry Department at Bramcote Hills Grammar.

In 1965 he migrated to Launceston, Tasmania, and was appointed to the Matriculation College there. He became Senior Master in 1967 and is a firm believer in the concept of the matriculation college.

A member of the Schools Board Syllabus Committee for Chemistry, Mr Calcraft is at present actively engaged in the trialling of CHEM Study in Tasmania. His work on a linear programme on elementary carbon chemistry has been published.

Mr Calcraft's main outside interests are brass banding, soccer and philately.

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